

# Towards the search of electron electric dipole moment: correlation calculations of the P,T-violation effect in the $\text{Eu}^{++}$ cation.

L.V. Skripnikov,<sup>1,\*</sup> A.V. Titov,<sup>1</sup> A.N. Petrov,<sup>1,†</sup> N.S. Mosyagin,<sup>1</sup> and O.P. Sushkov<sup>2</sup>

<sup>1</sup>*Petersburg Nuclear Physics Institute, Gatchina, Leningrad district 188300, Russia*

<sup>2</sup>*School of Physics, University of New South Wales, Sydney 2052, Australia*

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Recently the  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  solid was suggested as a promising candidate for experimental search of the electron electric dipole moment. To interpret the results of this experiment one should calculate the effective electric field acting on an unpaired (spin-polarized) electrons of europium cation in the crystal because the value of this field cannot be measured experimentally. The  $\text{Eu}^{++}$  cation is considered in the paper in the uniform external electric field  $E_{\text{ext}}$  as our first and simplest model simulating the state of europium in the crystal. We have performed high-level electronic structure correlation calculation using coupled clusters theory (and scalar-relativistic approximation for valence and outer core electrons at the molecular pseudopotential calculation stage that is followed by the four-component spinor restoration of the core electronic structure) to evaluate the enhancement coefficient  $K = E_{\text{eff}}/E_{\text{ext}}$  (where  $E_{\text{ext}}$  is the applied external electric field and  $E_{\text{eff}}$  is the induced effective electric field acting on an unpaired electron in  $\text{Eu}^{++}$ ). A detailed computation analysis is presented. The calculated value of  $K$  is -4.6.

## INTRODUCTION

During the past decades a significant experimental and theoretical efforts have been undertaken to measure an electric dipole moment of the electron ( $e\text{EDM}$  or  $d_e$  below).  $e\text{EDM}$  is of fundamental importance for theory of P,T-odd interactions because its existence violate both space parity (P) and time reversal (T) symmetries [1, 2]. The Standard model prediction for  $e\text{EDM}$  is of order  $10^{-38}e\text{-cm}$  of magnitude or even less, but the most of other modern theoretical models predict much higher values, on the level of  $10^{-27} - 10^{-29}e\text{-cm}$  [2]. Current experimental upper bound for  $e\text{EDM}$  is obtained in the measurements on the atomic Tl beam [3] and constitutes  $1.6 \cdot 10^{-27}e\text{-cm}$ . Therefore, increasing the experimental sensitivity on even one-two orders of magnitude for the value of  $e\text{EDM}$  will dramatically influence all the popular models suggesting a “new physics” beyond the Standard model, in particular supersymmetry, even if bounds on the P,T-odd effects compatible with zero are obtained (see [4, 5] and references therein).

Nowadays there are several experimental setups that are using molecules containing heavy atoms to measure  $e\text{EDM}$ . These include neutral molecule experiments, e.g., the beam experiment on the YbF molecular radicals carried on by Hinds and co-workers [6]; another one employs vapor cell in experiment on the metastable  $a(1)$  state of PbO that is prepared by the group of DeMille (see [7, 8] and references therein), the Stark-trap experiment on the PbF radicals is prepared by Shafer-Ray [9, 10] and some new beam experiments are now prepared on the metastable  $^3\Delta_1$  state of ThO\* [11] and the ground  $^3\Delta_1$  state of WC. In the other series of experiments suggested by Cornell and co-workers some trapped cold molecular cations are planned to be used. Up to now several cations were considered including  $\text{HI}^+$ ,  $\text{HfF}^+$ ,  $\text{PtH}^+$ ,  $\text{ThF}^+$ , etc.

(see [12] and references).

The ideas to use solids for such experiments were proposed by Shapiro many years ago [13]. However, only during the last decade such experiments to search for  $e\text{EDM}$  have become attractive due to suggestions of Lamoreaux [14] and Hunter [15] to use GdGaO and GdFeO. Recently a new kind of solid-state experiment was proposed on the  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  (EBTO) crystal [16] having perovskite structure. In this crystal Eu has seven unpaired spin-aligned electrons in 4f-shell and, therefore, nonzero magnetic moment. Besides, EBTO has ferroelectric phases at low temperatures [17]. This experiment (as well as the atomic and molecular experiments) employs the idea [18] that the electron EDM has to point along its magnetic moment (spin). As a result, when an electric field,  $E_{\text{ext}}$ , is applied to a sample lifting the degeneracy between electrons with EDMs parallel and antiparallel to  $E_{\text{ext}}$ , the associated imbalance of electron populations generates a magnetization [17]. The orientation of the magnetization is reversed when the electric field direction is switched; and this change in sample magnetization is supposed to be monitored using a SQUID magnetometer.

However, to extract the value of  $d_e$  it is necessary to know the value of the effective electric field acting on the unpaired electrons of Eu in  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  [16] which can not be measured. This is very difficult computational problem even for a solitary  $\text{Eu}^{++}$  cation (see below) and this paper starts our *ab initio* studies of  $E_{\text{eff}}$  in the  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  crystal. Here we consider the computationally simplest model simulating the electronic structure of Eu in EBTO:  $\text{Eu}^{++}$  cation in an external electric field.

## METHODS

When an atom (ion) with the unpaired electrons is placed into the external electric field  $E_{\text{ext}}$ , the resulting effective field  $E_{\text{eff}}$  acting on an unpaired electron is proportional to the applied (weak-) field with the enhancement coefficient  $K$ :

$$E_{\text{eff}} = K \cdot E_{\text{ext}}$$

It was Sandars who discovered that P,T-odd effects can be strongly enhanced in heavy atoms due to the relativistic effects [19]. A very useful semiempirical expression for  $K \sim \alpha^2 Z^3$  is proposed in [20] that is well working for  $s, p$  electrons though it is questionable for  $f$  electrons.  $E_{\text{eff}}$  is given by [21–23]):

$$E_{\text{eff}} = \langle \Psi | \sum_i H_d(i) | \Psi \rangle, \quad (1)$$

$$H_d(i) = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{\sigma}_i \mathbf{E}(\mathbf{r}_i) \end{pmatrix}, \quad (2)$$

$\Psi$  is the wave function of the atom (ion) in an external electric field  $E_{\text{ext}}$ ;  $\mathbf{E}(\mathbf{r}_i)$  is the sum of electric fields from nuclei and electrons. The wavefunction must take account of the most part of the relativistic and relevant correlation effects (see below) of valence (and sometimes outer-core) electrons. These electrons are the most affected (polarized) by the applied electric field and dramatically influence on  $E_{\text{eff}}$ . The polarization of the inner-core electrons is usually negligible. These circumstances allow us to use a two-step technique, advanced by our group [23–27] and recently applied for calculation of  $E_{\text{eff}}$  in molecular systems [28, 29]. *At the first step* we exclude inactive inner-core orbitals from correlation calculation with the help of a very accurate generalized relativistic effective core potential method (GRECP) [30–32] to reduce computational efforts. Besides, the valence orbitals are smoothed in cores and this smoothing allows one to reduce the number of primitive Gaussian basis functions required for appropriate description of valence spinors in subsequent molecular calculations. Moreover, as an alternative to a four-component calculation with small components of Dirac bispinors one can perform two- or one-component calculation, i.e., with or without spin-dependent interactions (which can include Breit etc. terms additionally to the spin-orbit ones) for explicitly treated electron shells taken into account. This procedure dramatically reduces computation time with minimal loss of accuracy (the particular choice of the valence / core electron’s partitioning is dependent first of all on the electronic structure of considered system and then, on the accuracy required). It should be noted that the all-electron four-component calculations are much more

time and resource consuming for the same level of accuracy as highly accurate GRECP ones.

*At the second step*, when the GRECP calculation is performed (with or without accounting for the electron correlation), we restore the four-component core electronic structure of valence orbitals and, thus, the corresponding relativistic one-electron density matrix from the GRECP one. Using the restored density matrix one can easily calculate any one-electron properties (such as  $E_{\text{eff}}$ , hyperfine constants, etc.) which have the most contributions in the atomic core regions. We have chosen the coupled clusters (CC) approach as the main instrument to account for electron correlation because it has a number of advantages over the other methods (such as restricted active space SCF (RASSCF), configuration interaction (CI), and many-body perturbation theory, which were also used at the preliminary stage) for our purposes: rather quick convergence of the results for the property of our interest with increasing the level of accounting for the electron excitations; well suppressed spin contamination problem (this is especially valuable for  $\text{Eu}^{++}$  having seven unpaired electrons with the multiplicity equal to 8).

Finally, the most important aspect of the present calculation should be stressed. The operator (2) is nonzero only between the states of opposite parities, e.g.,  $s-p, p-d, f-d$ , etc. Moreover, the corresponding molecular orbitals (on which this mixing takes place) should be spin-polarized or singly-occupied, otherwise, the contribution from a “spin-up” matrix element is completely compensated by some corresponding “spin-down” matrix element. The  $\text{Eu}^{++}$  cation has the ground state electronic configuration  $[.]4s^2 4p^6 4d^{10} 5s^2 5p^6 4f_{\uparrow}^7$ . Therefore, in an external electric field one should expect polarization of  $4f_{\uparrow}$  unpaired electrons into unoccupied low-lying  $5d$  states. However such a mixing will not result in a big value of the enhancement coefficient  $K$  because  $4f$  and  $5d$  have very small amplitudes in the vicinity of the Eu nucleus, where the operator (2) (mainly the electric field from the Eu nucleus) is big. The  $K$  value magnitude a few orders higher may be expected in the case of  $s-p$  mixing which takes place, e.g., in heavy alkali metals, such as cesium with  $[Xe]6s^1$  configuration, or in  $p^1$ -elements like thallium with  $[Hg]6p^1$  configuration (or in a number of molecules such as  $\text{HfF}^+$  in the  $^3\Delta_1$  state where the  $s-p$  mixing is very large due to the internal structure asymmetry of polar molecules. However,  $\text{Eu}^{++}$  has no unpaired electrons in  $s$  or  $p$  states and contribution to  $K$  from the matrix element of operator 2 due to the spin-polarized mixing of these states may occur only at the third and higher orders of perturbation theory, when both the weak (P,T-odd) and external field are treated as perturbations together with the electron correlation effects [33]. Thus, though the  $s-p$  matrix elements of operator (2) are big, the coefficients in front of these elements in the case of  $\text{Eu}^{++}$  are to be small

and dramatically dependent on the quality of accounting for the electron correlation (see [34] as an example of strong influence of correlation effects). That is why the calculation of  $K$  for  $\text{Eu}^{++}$  is much more complicated as compared to study of the mentioned atoms and molecules with respect to the required quality of accounting for electron correlations. We do not account for the spin-orbit effects in this research and concentrate our attention on the dynamic correlations since our estimates show that spin-orbit contributions do not influence strongly on the  $E_{\text{eff}}$  value whereas simultaneous treatment of both spin-orbit and correlation effects crucially reduce the possibilities of accounting for important dynamic correlations (and can not be currently taken into account at the correlation level exploited in the paper).

## COMPUTATIONAL DETAILS

For  $\text{Eu}^{++}$  cation, 28 core electron GRECP (with  $1s - 3d$  electrons in core) was generated and used for subsequent correlation calculations. In order to check a reliability of our value for  $K$  we have performed a detailed analysis of approximations used in our calculations such as basis set completeness, required level of accounting for correlation, etc., that is given below. To perform the correlation calculations we have used MRCC [35, 36] and CFOUR [37] codes. To perform DFT calculations we have used US-GAMESS program package [38].

### Basis set generation

For the  $\text{Eu}^{++}$  cation the contracted correlation scheme of the basis set generation from papers [30–32] was used. This scheme assumes that any last added function does not change the energy of the most important transitions (describing the state of atom-in-a-molecule) more than some threshold ( $10 \text{ cm}^{-1}$  in this paper). The generated basis set includes six s-type, seven p-type, five d-type, four f-type and two g-type generally contracted Gaussian functions. To check the merits of the generated basis set for evaluating  $E_{\text{eff}}$ , a series of coupled clusters (CC) calculations with single and double amplitudes (CCSD) has been performed with increasing step by step the number of basis functions. The results are given in table I.

It is clear from table I that  $K$  in the  $\text{Eu}^{++}$  ion strongly depends on the number of basis functions, e.g., even the latest added sixth and seventh contracted correlation functions give significant contributions to  $K$ . It is clear from the comparison of (\*) and (\*\*) lines that for d-type and f-type functions one can keep only 4 and 3 functions, respectively. The inclusion of g-type functions in calculation gives negligible contribution to  $K$  (that is well understandable in context of the discussed above  $f - d$  mixing), therefore, they can be completely excluded from

TABLE I:  $K$  values calculated using the CCSD method and different basis sets. ns, np, nd, nf and ng - are the numbers of s-, p-, d-, f- and g- contracted Gaussian functions included in the corresponding basis set

ns	np	nd	nf	ng	K(CCSD)
2	2	4	3	0	-0.9
3	3	4	3	0	1.3
4	5	4	3	0	2.3
4	5	5	4	0	2.2
4	5	5	4	2	2.2
5	6	5	4	2	0.1
6	6	5	4	0	-1.3
6	6	4	3	0	-1.2
6	7	4	3	0	-3.0 (*)
6	7	5	4	0	-3.1 (**)
6	7	5	4	2	-2.8
14	14	5	4	0	-4.1 (Lbas)
20	20	5	4	0	-4.1
14	14	12	4	0	-4.4

the basis set.

Accounting for the highest sensitivity of  $K$  to  $s$  and  $p$  functions we have performed calculations with uncontracted  $s$  and  $p$  functions (14 s- and 14 p- primitive gaussians). To check that the basis set is complete enough regarding to evaluation of  $K$ , the calculations with 20 s- and 20 p- functions have also been performed. However, the magnitude of  $K$  did not change. The additional uncontracting the  $d$ -orbitals (12 primitive  $d$ -type gaussian functions) changes  $K$  value only by 7%. As the computational time and resources for highly correlation study, such as CC with single, double and triple amplitudes CCSDT, strongly depends on the number of basis functions, we have chosen basis set which contains 14 primitive s-gaussians, 14 primitive p-gaussians, 5 contracted d-gaussians and 4 contracted f-gaussians which give the “converged” value of  $K$ . Below we shall refer to this basis set as to LBas.

### Optimal external field strength

To compute the enhancement factor  $K$ , the linear dependence of  $E_{\text{eff}}$  with respect to the applied field  $E_{\text{ext}}$  is required and the following two circumstances have to be satisfied: (i) the field must be strong enough to reduce influence of computational errors (round-up etc.) on  $K$ ; (ii) the field must be weak enough to prevent significant perturbations of the electronic structure (the physical external field is very small in practice and only the first-order perturbation of the wave function, linear on  $E_{\text{ext}}$ , should be taken into account).

We have performed a series of the CCSD calculations and have found that the linearity is provided in a wide range including  $10^{-6} - 10^{-1} \text{ a.u.}$  and have chosen  $E_{\text{ext}} = 0.001 \text{ a.u.}$  for our further calculations.

### Choosing the correlation method

It is well known that the methods based on the unrestricted Hartree-Fock (UHF) reference are not free from the spin contamination problem. Therefore, we have performed coupled clusters calculations also with the restricted open-shell Hartree-Fock (ROHF) reference. In this case the spin contamination problem excluded at the level of the reference (but can arise at the coupled cluster treatment stage due to features of the used codes). Table II gives values of  $K$  calculated at different levels of correlation treatment.

TABLE II: Calculated  $K$  values with different correlation methods using UHF and ROHF references. Mean values of the square of spin  $\langle S^2 \rangle$  operator are given in brackets (for the octet multiplicity “clean”  $\langle S^2 \rangle = 15.75$  ).

method	reference	$K$	
		UHF [ $\langle S^2 \rangle$ ]	ROHF [ $\langle S^2 \rangle$ ]
CCSD		-4.1 [15.75033]	-4.6 [15.75026]
CCSDT		-4.6 [15.75000]	-4.6 [15.75000]
MP2		-4.4	-3.6
MP3		-2.5	-2.7
MP4		-5.5	—

One can see from this table that accounting for the iterative triple amplitudes within the UHF-CCSDT method increases the magnitude of  $K$  by less than 15% as compared to  $K$ , calculated at the UHF-CCSD level. ROHF-based CC methods give  $K = -4.6$  already at the CCSD level and inclusion of triples do not change  $K$  value[43]

From the values of the mean squared spin operator one can see that the spin-contamination problem is not dramatic already at the CCSD level and is negligible at the CCSDT level. All these facts are good arguments that our ultimate value for  $K$ ,  $-4.6$ , is reliable.

Table II also illustrates why we have chosen coupled clusters method. The Møller-Plesset (MP) perturbation theory is not converged for  $K$  even at the fourth order. *From the other hand this illustrates that the enhancement factor  $K$  is determined by rather high-orders of perturbation theory where Coulomb interaction between electrons (accounting for correlation) is considered as perturbation.*

Summarizing, it follows from the above analysis that the use of the CCSDT method is sufficient for reliable calculation of  $K$  and our final value is  $K = -4.6$ .

### ANALYSIS OF CONTRIBUTIONS TO $K$

It was mentioned above that one of stages of calculating  $K$  is evaluation of the spin density matrix. Therefore it is possible to estimate contributions from the mixing of the basis functions having different angular momenta by setting all of the other elements of the spin density

matrix to zero. By this way we have estimated such contributions to  $K$  from the spin density matrix calculated at the CCSDT level. The contributions are given in table III:

TABLE III: Pair contributions to  $K$  calculated at the CCSDT level.

	s	p	d	f
s	0	-3.3	0	0
p		0	+0.3	0
d			0	-1.6
f				0

It follows from this table that the main (cumulative) contribution to  $K$  is provided by the  $s - p$  mixing. The next important contribution (which is twice smaller) is provided by the  $f - d$  mixing. Contribution from the  $p - d$  mixing is almost negligible.

It is very instructive to estimate contributions to  $K$  from the individual (outer-core and valence)  $ns, np$  shells. Qualitatively, the spin exchange of a given  $ns_{\uparrow}$  or  $np_{\uparrow}$  orbital with  $(4f_{\uparrow})^7$ , lead to spin-polarization of the shells and, being space-polarized by  $E_{\text{ext}}$ , to uncompensated contribution to  $K$ . It is first dependent on the following two factors: (i) space localization relative to the  $4f$ -shell (which is occupied by seven alpha-spin electrons); (ii) energy separation relative to the polarizing orbitals whose energies, by order of magnitude, are close to zero. From table IV it can be seen that  $4s$  and  $4p$  orbitals are localized at the same region as  $4f$ -orbitals, at the same time last maxima of the  $5s$  and  $5p$  orbitals are in about 1.5 times larger. From the other hand,  $5s, 5p$  energy factors (denominators) are much smaller than those for the  $4s, 4p$ . In turn, the space polarization  $s - p$ ,  $p - d$  etc. due to the  $E_{\text{ext}}$  should be expected notably stronger for the  $5s$  and  $5p$  orbitals whereas matrix elements of (2) are smaller for them. Thus both  $5s, 5p$  as well as  $4s, 4p$  shells have to be included to the calculation. Their relative importance can be caught only in the calculation which must account for electronic correlation. In turn,  $3s$  and  $3p$  orbitals (and those with “lower”  $n$ ) have essentially different space localization (4.5 times smaller averaged radii) and too large energy denominator  $\sim 60$  a.u. Therefore, we do not consider these shells in the paper, particularly, because their explicit treatment dramatically increase the computational effort.

In order to estimate contributions from different shells we have performed a series of calculations at the CCSDT level with the ROHF reference calculated at zero external electric field. In these calculations we have frozen different orbitals, i.e., have forbidden their spin and space polarization. For every calculation we have also decomposed  $K$  on contributions going from the  $s - p$  ( $K_{s-p}$ ),  $p - d$  ( $K_{p-d}$ ), and  $f - d$  ( $K_{f-d}$ ) mixings. In paper [33], the  $\text{Gd}^{+++}$  system electronically equivalent to  $\text{Eu}^{++}$  was studied where the scheme of the  $s - p$  mixing with excita-

TABLE IV: averaged radii,  $\langle r \rangle$ , last maximum position,  $r_{max}$ , and orbital energies,  $\epsilon_{orb}$ , of  $\text{Eu}^{++}$  spin-orbit averaged spinors.

orbital	$\langle r \rangle$ , a.u.	$r_{max}$ , a.u.	$\epsilon_{orb}$ , a.u.
3s	0.2	0.3	-68.0
3p	0.2	0.3	-57.7
3d	0.2	0.3	-43.6
4s	0.6	0.5	-15.1
4p	0.6	0.5	-11.5
4d	0.7	0.6	-6.5
4f	0.9	0.6	-1.0
5s	1.4	1.3	-2.6
5p	1.6	1.4	-1.6

tions to unoccupied  $d$  states was considered. To analyze importance of other possible correlation schemes of the  $s-p$  mixing in  $\text{Eu}^{++}$  we have performed all these calculations in two basis sets: (i) our standard basis set Lbas (which has been used for previous calculations) and (ii) the Lbas\_nvd basis set which was derived from Lbas by keeping all the  $s$ ,  $p$ ,  $f$  and only one contracted  $4d$  function (taken from ROHF) and excluding all the other  $d$  functions. This means that no virtual  $d$ -orbitals will appear in Hartree-Fock calculations with the Lbas\_nvd basis (addition “nvd” means “No Virtual  $d$ ”). In such a way we have excluded virtual  $d$ -orbitals from the calculations. The results of the calculations are given in table V.

One can make many fruitful conclusions from this table, but we shall point out only at several of them:

(i)  $K_{s-p}$  contribution from the spin and space polarization (below we call the simultaneous effect as just the polarization) of  $5s$  and  $5p$  orbitals. To extract a “clean” contribution from polarization of the  $5s$  orbital we have frozen  $4s$ ,  $4p$ ,  $4d$  and  $5p$  orbitals, thus, only the  $5s$  and  $4f$  occupied shells were included in the correlation calculation (see line 3 in the table). The  $K_{s-p}$  value for this case in Lbas is  $+1.2$ . The case with excluded virtual  $d$ -basis functions (using Lbas\_nvd basis) gives  $K_{s-p} = +0.8$ . Therefore, one can conclude that the mechanism of polarization of the  $5s$ -orbital including intermediate excitation into virtual  $d$ -orbitals (being large in lowest PT orders as is shown in [33]) is suppressed in the higher PT orders and, therefore, can not be considered as the leading one. Moreover, as the  $4d$  shell is frozen in this calculation the contribution originates from the spin-polarization (by seven electrons occupying  $4f_{\uparrow}$ -orbitals) of the occupied  $5s$ -orbital directly and indirectly, by means of the virtual  $p$  states, that is complemented by the space polarization of these  $5s$  states into virtual  $p$ -states.

“Clean” contribution from polarization of the  $5p$ -orbitals (below will write just as contributions of  $5p$  for brevity, etc.) to  $K_{s-p}$  is  $-0.9$  (that includes intermediate virtual  $s$ ,  $p$ , and  $d$  functions, see line 4). Note that the nvd mechanism gives  $K_{s-p} = +2.1$ . Both polarizations of  $5s$  and  $5p$  orbitals give significant contributions, however,

these terms have opposite signs and simultaneous correlation of  $5s$  and  $5p$  orbitals (see line 5 of the table) results in almost negligible  $K_{s-p}$  value,  $+0.2$  (note that the sum of the partial  $5s$  ( $+1.2$ ) and  $5p$  ( $-0.9$ ) contributions is  $+0.3$ , therefore, they are practically additive). It should be noted that the nvd-mechanism gives  $K_{s-p} = +2.0$ , therefore, it looks like that there is almost exact compensation between contributions with intermediate virtual  $s$ ,  $p$  and virtual  $d$  states. Additional inclusion of  $4d$  orbitals in the correlation calculation (line 6) leads to decrease of  $K_{s-p}$  by  $1.0$ .

(ii)  $K_{s-p}$  contribution from the polarization of  $4s$  and  $4p$  orbitals. From lines 7, 8 and 9 one can see that the individual polarization contributions to  $K_{s-p}$  from the  $4s$  and  $4p$  orbitals are slightly higher (by absolute value) than the corresponding  $5s$  and  $5p$  contributions, and, in turn, they have the same signs which leads to big final  $K_{s-p}$ ; also both  $4s$  and  $4p$  polarizations are mainly due to the “virtual  $d$ ” mechanism and they are also almost additive. Additional inclusion of  $4d$ -orbitals in the correlation calculation (line 10) leads to decrease of  $K_{s-p}$  by  $0.5$ . At last, it is the polarization of  $4s$  and  $4p$  orbitals that gives the *leading* contribution to the final  $K_{s-p}$  and total  $K$  values.

(iii) Simultaneous correlation of  $4s$ ,  $4p$ ,  $5s$ ,  $5p$  (and, of course,  $4f$ ) orbitals (line 11) leads to certain decrease of  $K_{s-p}$  by absolute value with respect to the sum of  $4s$ ,  $4p$  and  $5s$ ,  $5p$  contributions. Here we have new types of “interfering polarization contributions” e.g., between  $4s$  and  $5p$ ,  $4p$  and  $5s$ , etc. Additional inclusion of  $4d$ -orbitals in the correlation calculation (line 1) leads to further decrease of the  $K_{s-p}$  value by  $1.5$ .

(iv)  $K_{f-d}$  notably depends on the  $5p$  orbital (compare lines 2 and 4). One can expect that this is mainly due to the space  $5p-5d$  polarization (together with the spin-polarization to intermediate virtual  $d$  states) that decrease the contribution from the direct (lowest order) space  $4f-5d$  polarization.

(v) The polarization of  $5p$  to virtual  $d$  (lines 2, 4) and of  $4d$  to virtual  $p$  orbitals (lines 2, 12), as well as the small term with polarization of  $4p$  to virtual  $d$  (lines 2, 8) have the opposite signs (and small magnitudes) resulting in a negligible final value of  $K_{p-d}$  (line 1).

One important note should be made for the  $K_{f-d}$  contribution. The amplitude of the  $f$  function is very small at the core region of  $\text{Eu}^{++}$ . Therefore, it is important to take into account the electric field screening effect from the core shells. We have calculated that neglecting these screening effects leads to 25% overestimation of the  $K_{f-d}$  contribution. Also, it should be noted that all the core shells give screening effects, i.e. not only  $1s$ , but  $2s-3d$  give essential contribution there as well.

It is clear from table V that mechanisms of forming the final enhancement factor value  $K$  are very complicated, and one should consider many orders of perturbation theory by interelectronic Coulomb interaction (as expected

TABLE V: Calculated  $K$  values and its components using the ROHF-CCSDT method (The ROHF-reference is taken from zero  $E_{\text{ext}}$  field calculation to prevent space polarization of the orbitals to be frozen).

#	Active orbitals	Frozen orbitals	Lbas				Lbas_nvd			
			$K$	$K_{s-p}$	$K_{p-d}$	$K_{f-d}$	$K$	$K_{s-p}$	$K_{p-d}$	$K_{f-d}$
1	all	-	-4.7	-3.4	0.3	-1.7	1.6	1.8	0.0	-0.3
2	$4f$ — only	$4s4p4d5s5p$	-1.8	0.0	0.0	-1.8	0.0	0.0	0.0	0.0
3	$5s, 4f$	$4s4p4d\_5p$	-0.6	1.2	0.0	-1.8	0.8	0.8	0.0	0.0
4	$5p, 4f$	$4s4p4d5s\_$	-1.3	-0.9	0.8	-1.2	2.1	2.1	0.0	0.0
5	$5s\&5p, 4f$	$4s4p4d\_$	-0.3	0.2	0.8	-1.3	2.0	2.0	0.0	0.0
6	$4d\&5s\&5p, 4f$	$4s4p\_$	-1.9	-0.8	0.6	-1.7	1.3	1.5	0.0	-0.3
7	$4s, 4f$	$\_4p4d5s5p$	-3.7	-1.9	0.0	-1.8	0.0	0.0	0.0	0.0
8	$4p, 4f$	$4s\_4d5s5p$	-3.2	-1.1	-0.3	-1.8	0.1	0.1	0.0	0.0
9	$4s\&4p, 4f$	$\_4d5s5p$	-5.4	-3.3	-0.3	-1.8	0.1	0.1	0.0	0.0
10	$4s\&4p\&4d, 4f$	$\_\_5s5p$	-6.8	-3.8	-0.7	-2.2	-0.1	0.1	0.0	-0.2
11	$4s\&4p\&5s\&5p, 4f$	$\_\_4d\_$	-2.5	-1.9	0.6	-1.3	2.3	2.3	0.0	0.0
12	$4d, 4f$	$4s4p\_5s5p$	-2.7	0.0	-0.4	-2.2	-0.2	0.0	0.0	-0.2

from the qualitative discussion in section “Methods”). As is stressed above, it is the coupled clusters theory which includes many orders of perturbation theory that we have chosen for our calculation. This is the only method that allowed us to attain convergent results for such a complicated problem as evaluating  $K$  in lanthanides.

## DENSITY FUNCTIONAL AND MØLLER-PLESSET ESTIMATES

As was mentioned above this paper is the first one in our studies of  $E_{\text{eff}}$  on  $\text{Eu}^{++}$  having in mind to describe the effective state of Eu in the crystal  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  as our final goal. Since in solid-state calculations one cannot use such methods as coupled clusters we have calculated  $K$  using the Møller-Plesset perturbation theory (see table II above) and different popular exchange-correlation functionals. Although the second order Møller–Plesset perturbation theory with the UHF-reference is in a good agreement with our final value of  $K$  (and even individual  $s - p$ ,  $p - d$  and  $f - d$  contributions are so as well) for the system under consideration, however we cannot consider the UHF–MP2 values as reliable enough because the ROHF–based MP2, as well as the UHF– and ROHF–based MP3 and MP4 values are seriously divergent from them demonstrating instability of the MP series. Thus, one can try to use MP2 (mainly for many-atomic systems) but with great caution.

Unfortunately, there are no reliable theoretical criteria to choose the most appropriate DFT exchange-correlation functional versions for a problem of the considered type because it is impossible to perform a series of successive DFT calculations with consistent increase of the level of accuracy of theory to achieve convergence as it can be done, at least formally, in the framework of the explicitly-correlated ab initio methods (see above). Therefore the only a way to choose density functional is to “calibrate” it comparing to a high-level correlation calculations. In table VI we present the calculated  $K$  values using different exchange-correlation functionals. One should note that  $K_{s-p}$ ,  $K_{p-d}$  and  $K_{f-d}$  have the same weights as in the case of CCSDT.

TABLE VI: Calculated  $K$  values using popular exchange-correlation functionals.

Functional	$K$
PBE [39]	-3.7
TPSS [40]	-3.8
B3LYP [41]	-2.9
PBE0 [42]	-2.7

## CONCLUSION

The  $\text{Eu}^{++}$  cation in an external electric field has been considered as the simplest important model that simulates effective state of europium in our studies of the EBT crystal properties. The calculated enhancement factor is  $K = -4.6$ . It is shown that this value is not well determined by even the lowest four orders of the many-body perturbation theory by the Coulomb operator, so the coupled-cluster expansion for the wave function is important to attain a convergence for this value. The other exploited methods including the RASSCF and CI ones did not allow us to attain the convergence on  $K$  in a reasonable time using available computer resources. The main contribution to  $K$  originates from the spin-space polarization of  $s$  and  $p$  occupied orbitals.

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\* Electronic address: leonidos239@gmail.com

† Also at St.-Petersburg State University, St.-Petersburg, Russia

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